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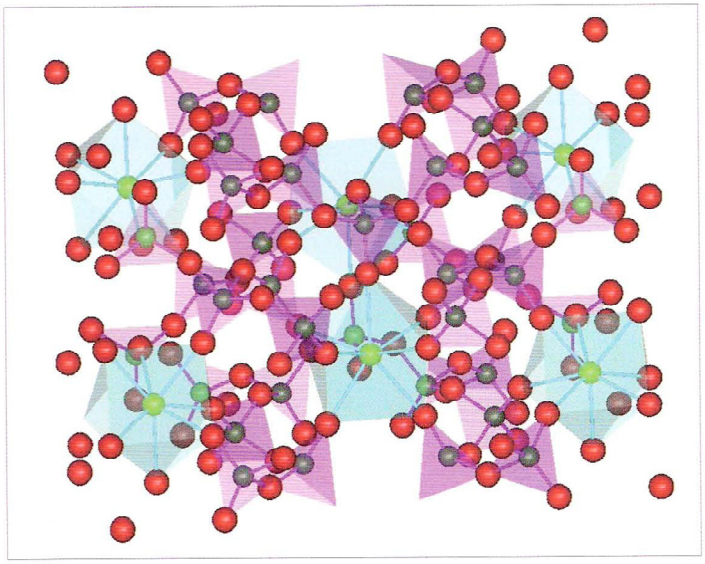
Structure of rare-earth phosphate glass studied by anomalous dispersion neutron diffraction

Rare-earth (R) phosphate glasses $(R_2O_3)_x{\cdot}(P_2O_5)_{1-x}$ where x = 1/4 or 1/6 have shown great promise in the laser and optoelectronics industry. This is because the rare-earth ions possess the required energy levels for achieving successful population inversion and the non-linear refractive index is large enough to exhibit the desired optical effects without causing beam breakup and damage. Moreover, the particularly high concentration of rare-earth ions present in these materials results in a myriad of exotic physical properties at low temperatures: negative thermal expansion, negative pressure dependence of bulk moduli and unprecedented magnetic, magneto-optical and opto-acoustic phenomena [1].



The structural nature of these glasses dictates their physical properties, especially the closest R…R approach, since too close a separation impairs their optical and magnetic phenomena. Conventional X-ray [4-8] and neutron diffraction, X-ray absorption spectroscopy, and solid-state NMR studies have, in combination, been able to piece together a model of the local structure of these glasses, out to an interatomic distance, r, of about 4 Å (see **figure 1**). However, the R…R separation is not part of this defined local structure, and beyond this ~4 Å radial limit conventional characterisation techniques are uninformative owing to (i) increasing numbers of overlapping pair-wise correlations in conventional diffraction; (ii) the progressively damped signal, and obscuring multiple scattering effects in X-ray absorption spectroscopy; (iii) the inherent short-range J-J coupling effects in NMR, and heavily broadened signal due to the paramagnetic nature of rare-earth ions.

One must therefore turn to non-conventional diffraction techniques to determine the nearest R...R separation. Samarium has a physical characteristic, unique to all rare earths, that makes it ideal for use in such a non-conventional diffraction experiment, which yields R···R correlations exclusively in one part, and R···X and X···X correlations (X is any element that is not R) in another part. This is the anomalous neutron dispersion effect associated with the ^{149}Sm isotope, which is 14% naturally abundant in samarium. It is this physical characteristic that we exploit here in performing an anomalous dispersion neutron diffraction experiment on vitreous $Sm_2O_3 \cdot 4P_2O_5$ [2].

The anomalous dispersion technique is employed successfully with X-rays at synchrotron radiation sources, which provide the required incident intensity and sufficiently dynamic energy spectrum that encompasses the required absorption edge as well as an energy void of all resonant effects. The equivalent neutron technique involves the variation in the neutron scattering length with wavelength around an absorption resonance, $b = b^0 + b'(\lambda) + i\,b''(\lambda)$, $b'(\lambda)$ and $b''(\lambda)$ being the wavelength-dependent real and imaginary parts of the scattering length, usually arising from a single isotope of the element in question; b^0 is the wavelength-independent contribution to the scattering length from all of the isotopes present. The relative change in the scattering length for neutrons is very much larger than that in the atomic form factor for x-rays. This, together with the greatly enhanced

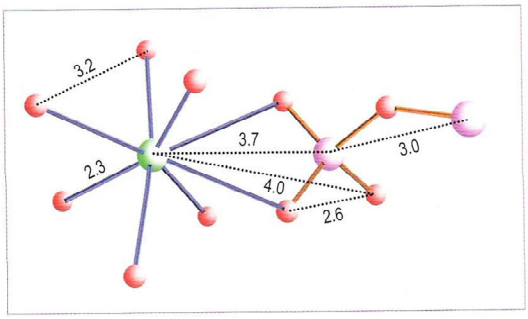


***Figure 1**: A model of rare-earth meta-phosphate glass. Green, red, and purple spheres represent the rare-earth, oxygen and phosphorus atoms, respectively. The dashed lines represent possible coordination levels since that of the rare-earth varies from 6 to 8 depending on the glass stoichiometry. The numbers represent interatomic distances in Å.*

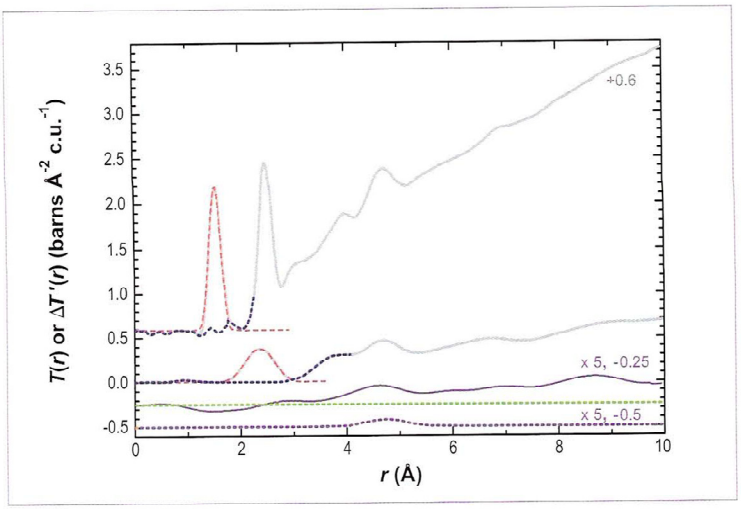


***Figure 2**: T(r) for the 0.45 Å data, together with the fit to the first (P-O) peak (top curves shifted by +0.6); ΔT'(r) plus the fit to the Sm-O peak (middle curves); (gray curves: data; red curves: fit; blue curves: residuals). ΔT''(r) together with the simulated peak for Sm...Sm pairs based on a linear Sm-O-Sm arrangement (orange curves). The bottom mauve curves are calculated using a Q_{max} of 7 $Å^{-1}$ and are scaled by a factor of five and shifted by -0.25 and -0.5; the dotted green line is zero.*

cross-section in the region of the absorption resonance, means that it is possible to perform measurements at the peak of the resonance.

The judicious choice of four wavelength measurements allows one to exploit both the real and imaginary components of b_{Sm} in an anomalous dispersion neutron diffraction experiment, such that one can obtain not only a spectrum comprising the Sm···Sm and Sm···X components, but also one comprising the Sm···Sm correlations exclusively. Due to the highly involved technical and analytical nature of this investigation, further technical details of this study are presented in [3].

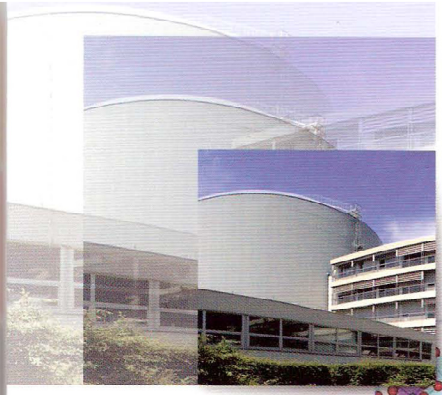
Results show (**figure 2**) that vitreous $Sm_2O_3 \cdot 4P_2O_5$ comprises a mixed network of SmO_n polyhedra and PO_4 tetrahedra. The Sm^{3+} ions have an average co-ordination number of 7, which corroborates prior complementary X-ray diffraction, L-edge and K-edge EXAFS results. This confirms our previously held knowledge about the basic phosphate network and rare-earth environment; such corroboration is extremely useful for the verification of this study given its complexity. The mean Sm–O bond length is 2.375(5) Å. The ability to draw out Sm···X + Sm···Sm correlations exclusively via the first-order difference, $\Delta T'(r)$ affords excellent accuracy in the determination of these Sm–O correlation parameters; in conventional diffraction, Sm–O and O–(P)–O correlations overlap. The anomalous difference correlation function, $\Delta T''(r)$, suggests that most of the Sm^{3+} ions are separated from each other on average 4.8 Å apart. By calculations based on the R–O correlation, we have shown that the $\Delta T'(r)$ and $\Delta T''(r)$ results, which yield the main R···R peak, are mutually consistent. There is evidence of a closer Sm···Sm separation nearer to 4 Å, and other Sm···Sm correlations at around 5.9 and 6.9 Å. A peak with a very wide distribution (of nearly 2 Å) is centred at 8.8 Å. The fact that there is clear evidence for Sm···Sm correlations below those anticipated for a random distribution of Sm^{3+} ions means that local clusters of Sm^{3+} ions must be present in the structure. This information will help in producing more comprehensive structural models so that one can relate better to the optical and magnetic properties of these materials.

References

[1] J. M. Cole *et al.*, J. Phys.: Condens. Matter 11 (1999) 9165; *ibid.* 13 (2001) 6659

[2] J. M. Cole *et al.*, J. Phys.: Condens. Matter 19 (2007) 056002

[3] A. C. Wright *et al.*, Nucl. Instr. Meth. A 571 (2007) 622



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